UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2008/2009

June 2009

KOT 323 – Organic Chemistry III
[Kimia Organik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **EIGTHTEEN** printed pages before you begin the examination.

Instructions:-

Answer **FIVE** (5) questions.

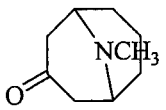
Answer each question on a new page.

You may answer either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

...2/-

1. Give the structures of the products **A** through **J:**



$\xrightarrow{NaBH_4}$ **A** ($C_9H_{17}ON$)

A + heat $\longrightarrow$ **B** ($C_9H_{15}N$)

B + CH_3I, then Ag_2O $\longrightarrow$ **C** ($C_{10}H_{19}ON$)

C + heat $\longrightarrow$ **D** ($C_{10}H_{17}N$)

D + CH_3I, then Ag_2O $\longrightarrow$ **E** ($C_{11}H_{21}ON$)

E + heat $\longrightarrow$ **F** (C_8H_{10})

F + Br_2 $\longrightarrow$ **G** ($C_8H_{10}Br_2$)

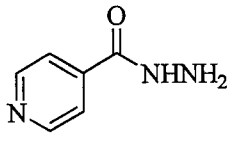
G + $(CH_3)_2NH$ $\longrightarrow$ **H** ($C_{12}H_{22}N_2$)

H + CH_3I, then Ag_2O $\longrightarrow$ **I** ($C_{14}H_{30}O_2N_2$)

I + heat $\longrightarrow$ **J** (C_8H_8)

(20 marks)

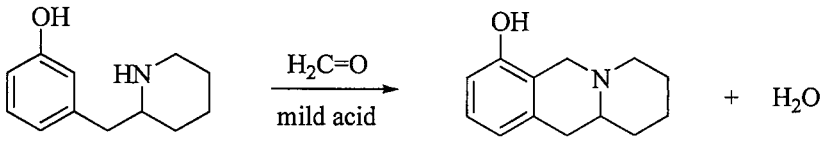
2. (a) Rank the nitrogen atoms in isoniazid (**K**) in order of increasing basicity, justifying your answer,



(K)

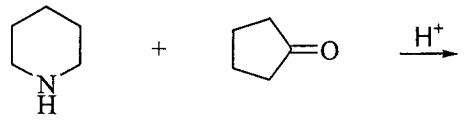
(3 marks)

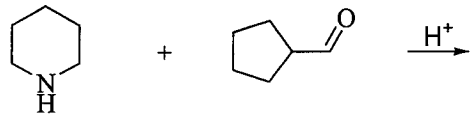
(b) Draw a stepwise mechanism for the following reaction:

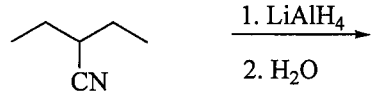


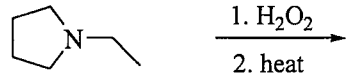
(5 marks)

(c) Draw the organic products formed in each of the reactions below:

(i) 

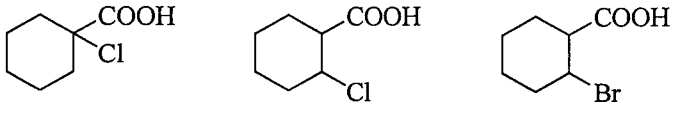
(ii) 

(iii) 

(iv) 

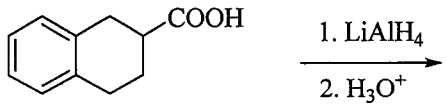
(12 marks)

3. (a) Arrange the following compounds in order of increasing acidity giving reasons for your choice.

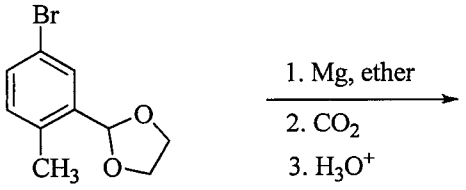


(3 marks)

(b) Predict the products of the following reactions:

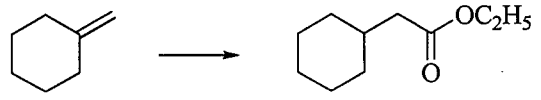
(i) 

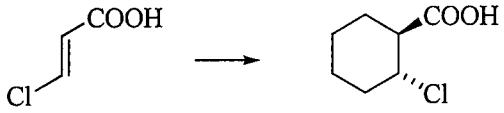
(ii) 

(iii) 

(9 marks)

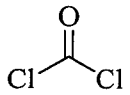
(c) Show how you could accomplish the following synthesis. You may use any necessary reagents.

(i) 

(ii) 

(8 marks)

4. (a) Phosgene (**L**) is the acid chloride of carbonic acid.



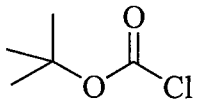
(L)

Predict the products found when phosgene reacts with:

(i) Excess ethanol.
(ii) Excess methylamine.
(iii) 1 equivalent of methanol, followed by 1 equivalent of aniline.
(iv) Ethylene glycol ($HOCH_2CH_2OH$).

(6 marks)

(b) *t*-Butyloxycarbonyl chloride (**M**) is an important reagent in the synthesis of peptides and proteins. Show how you would use phosgene to synthesize (**M**).

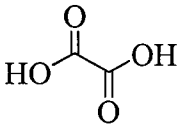


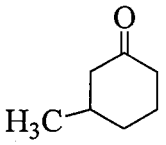
(M)

(4 marks)

(c) Give the structures of **N-T** in the reactions below;

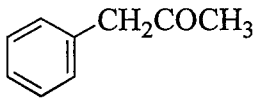
(i) $CH_3CH_2COOH \xrightarrow{PBr_3/Br_2}$ **N**

(ii)  $\xrightarrow{PBr_3/Br_2}$ **Q**

(iii)  $\xrightarrow[H^+]{}$ **R** $\xrightarrow{CH_3COCl}$ **S** (acyl iminium salt) $\xrightarrow{H_3O^+}$ **T**(β-diketone)

(10 marks)

5. (a) Phenylacetone **U** can form two different enols.

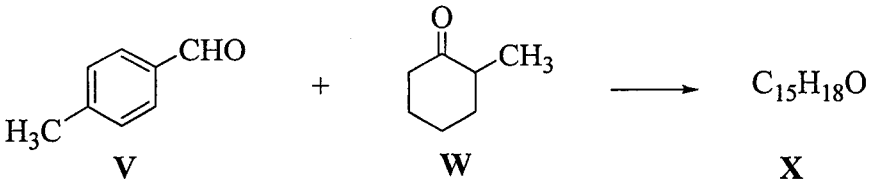


U

(i) Show the structures of these enols.
(ii) Which one is more stable? Give your reason?
(iii) Propose mechanism for the formation of these enols in acid.

(8 marks)

(b) Treatment of the aldehyde **V** and ketone **W** with sodium acetate would give compound **X** with molecular formula $C_{15}H_{18}O$.



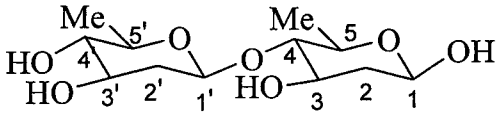
V **W** **X**

(i) Draw the structure of **X**.

(ii) Show the mechanism of the reaction.

(6 marks)

(c) The structure of cyclic hemiacetal form of disaccharide is shown below:

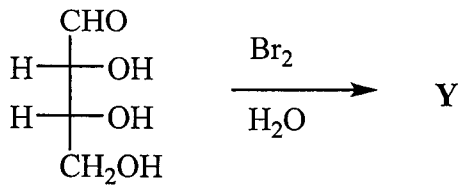


(i) Which is the anomeric carbon of this structure? What is the type of anomer that this disaccharide show?.
(ii) What type of glycosidic linkage is shown by this disaccharide?.

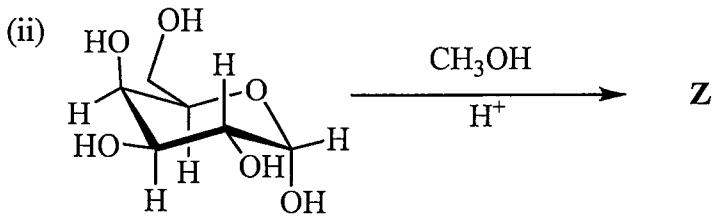
(6 marks)

6. (a) Draw the structures of **Y** and **Z**.

(i)

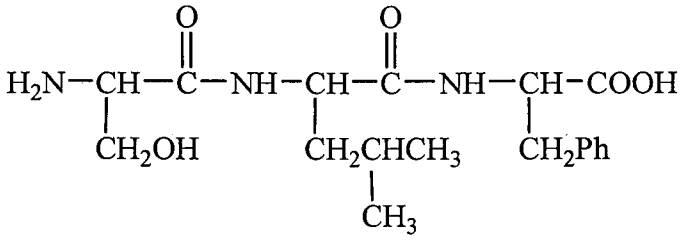


(ii)



(4 marks)

(b) Show the synthetic steps of Ser-Leu-Phe by using solution-phase method.



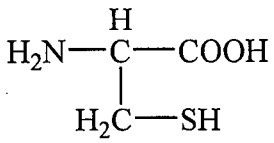
Ser-Leu-Phe

(10 marks)

(c) Complete hydrolysis of a hexapeptide gave 2 Gly, Leu, Phe, Pro. and Tyr. Reaction of the peptide with phenylisothiocyanate gave the phenylthiohydantoin of Pro. Partial hydrolysis of the peptide gave the following fragments: Phe-Gly-Tyr, Gly-Phe-Gly, Pro-Leu-Gly, Leu-Gly-Phe. What is the structure of the peptide?

(6 marks)

7. (a) Show how you would synthesize cysteine from:



cysteine

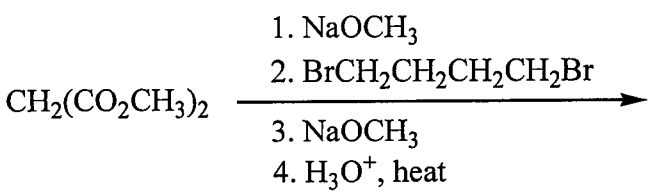
(i) Reductive amination.

(ii) Strecker synthesis.

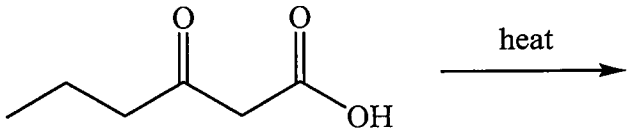
(10 marks)

(b) Predict the major organic products of the following reactions:

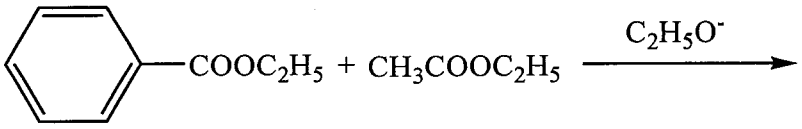
(i)



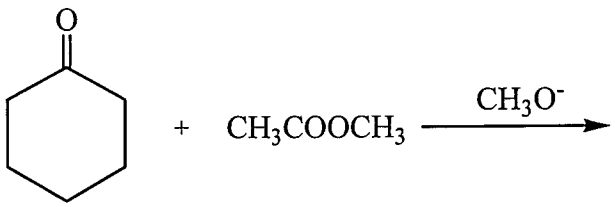
(ii)



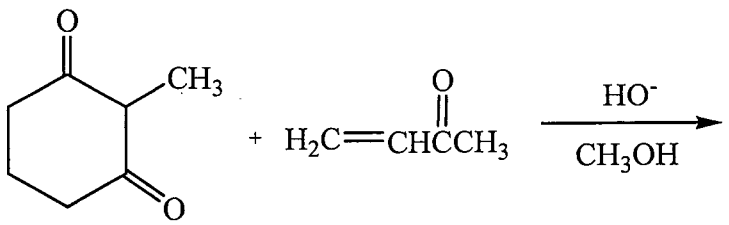
(iii)



(iv)



(v)



(10 marks)

TERJEMAHAN

Arahan:-

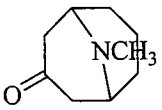
Jawab **LIMA** (5) soalan.

Jawab setiap soalan pada muka surat yang baru.

Anda boleh menjawab sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

1. Berikan struktur bagi hasil **A** hingga **J**:



$\xrightarrow{NaBH_4}$ **A** $(C_9H_{17}ON)$

A + pemanasan $\longrightarrow$ **B** $(C_9H_{15}N)$

B + CH_3I, kemudian Ag_2O $\longrightarrow$ **C** $(C_{10}H_{19}ON)$

C + pemanasan $\longrightarrow$ **D** $(C_{10}H_{17}N)$

D + CH_3I, kemudian Ag_2O $\longrightarrow$ **E** $(C_{11}H_{21}ON)$

E + pemanasan $\longrightarrow$ **F** (C_8H_{10})

F + Br_2 $\longrightarrow$ **G** $(C_8H_{10}Br_2)$

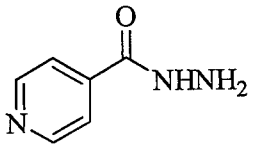
G + $(CH_3)_2NH$ $\longrightarrow$ **H** $(C_{12}H_{22}N_2)$

H + CH_3I, kemudian Ag_2O $\longrightarrow$ **I** $(C_{14}H_{30}O_2N_2)$

I + pemanasan $\longrightarrow$ **J** (C_8H_8)

(20 markah)

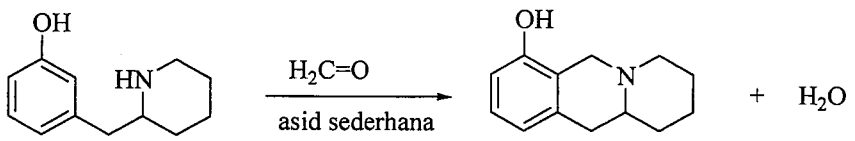
2. (a) Susunkan atom nitrogen di dalam isoniazid (**K**) mengikut tertib kebesan yang meningkat. Jelaskan jawapan anda.



(K)

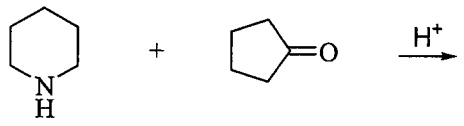
(3 markah)

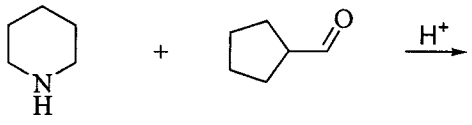
(b) Lukiskan suatu mekanisme, langkah demi langkah, bagi tindak balas berikut:

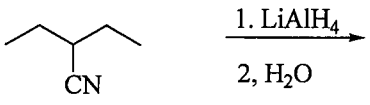


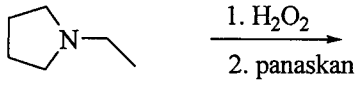
(5 markah)

(c) Lukiskan hasil organik yang terbentuk di dalam setiap tindak balas berikut:

(i) 

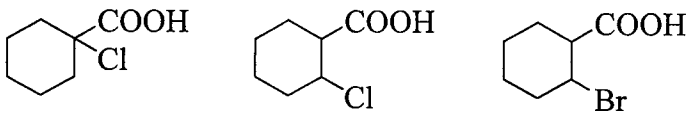
(ii) 

(iii) 

(iv) 

(12 markah)

3. (a) Susunkan sebatian berikut mengikut tertib keasidan yang meningkat. Berikan alasan untuk menjelaskan jawapan anda.

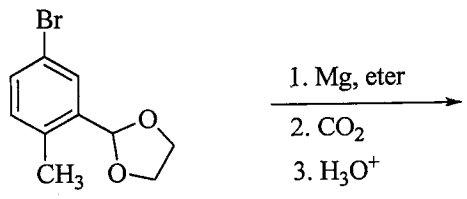


(3 markah)

(b) Ramalkan hasil tindak balas berikut:

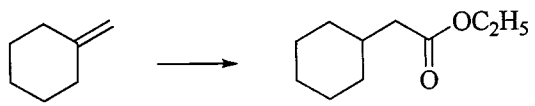
(i) 

(ii) 

(iii) 

(9 markah)

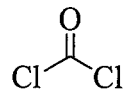
(c) Tunjukkan cara untuk mencapai setiap sintesis berikut. Anda boleh menggunakan sebarang reagen yang diperlukan.

(i) 

(ii) 

(8 markah)

4. (a) Fosgena (**L**) ialah asid klorida daripada asid karbonik.



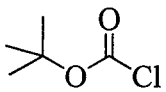
(L)

Ramalkan hasil yang terbentuk apabila fosgena bertindak balas dengan:

(i) Etanol berlebihan
(ii) Metilamina berlebihan
(iii) 1 equivalen metanol, diikuti dengan 1 equivalen anilina
(iv) Etilena glikol ($HOCH_2CH_2OH$)

(6 markah)

(b) *t*-Butiloksikarbonil klorida (**M**) ialah suatu reagen penting dalam sintesis peptida dan protein. Tunjukkan bagaimana **(M)** dapat disintesiskan daripada fosgena.

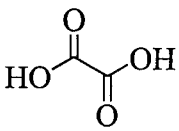


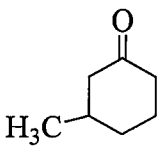
(M)

(4 markah)

(c) Berikan struktur **N-T** dalam tindak balas dibawah.

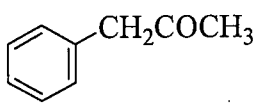
(i) $CH_3CH_2COOH \xrightarrow{PBr_3/Br_2}$ **N**

(ii)  $\xrightarrow{PBr_3/Br_2}$ **Q**

(iii)  $\xrightarrow[H^+]{}$ **R** $\xrightarrow{CH_3COCl}$ **S** (garam iminium asil) $\xrightarrow{H_3O^+}$ **T** (β-diketon)

(10 markah)

5. (a) Fenilaseton **U** boleh membentuk dua enol yang berbeza.

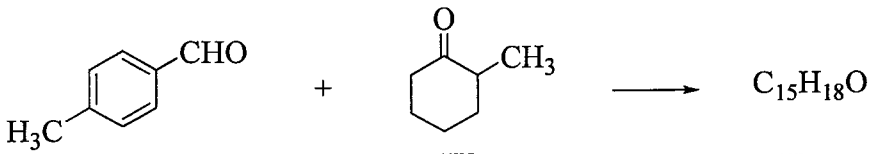


U

(i) Tunjukkan struktur enol tersebut.
(ii) Yang manakah lebih stabil? Berikan alasan.
(iii) Cadangkan mekanisme untuk pembentukan enol tersebut dalam asid.

(8 markah)

(b) Pengolahan aldehid **V** dan keton **W** dengan natrium asetat akan memberikan sebatian **X** dengan formula molekul $C_{15}H_{18}O$.

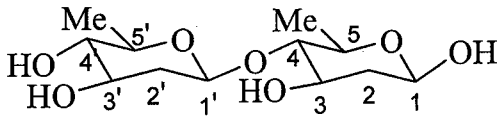


V **W** **X**

(i) Lukiskan struktur **X**
(ii) Tunjukkan mekanisme tindak balas

(6 markah)

(c) Struktur bentuk hemiasetal siklik disakarida ditunjukkan di bawah:



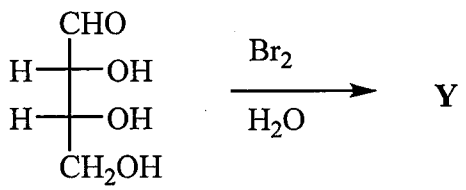
(i) Yang manakah karbon anomerik pada struktur ini?. Apakah jenis anomer yang ditunjukkan oleh disakarida ini?
(ii) Apakah jenis pengikatan glikosidik yang ditunjukkan oleh disakarida ini?.

(6 markah)

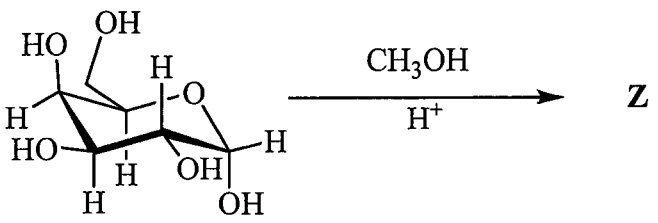
...16/-

6. (a) Lukiskan struktur **Y** dan **Z**.

(i)

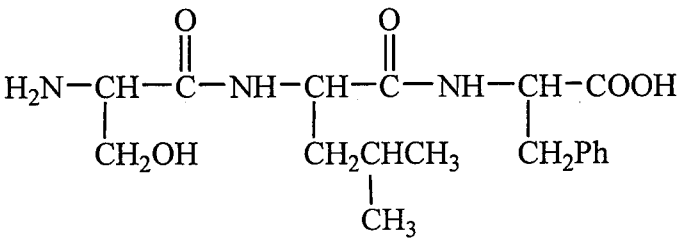


(ii)



(4 markah)

(b) Tunjukkan langkah sintesis bagi Ser-Leu-Phe dengan menggunakan kaedah fasa larutan.



Ser-Leu-Phe

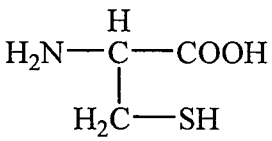
(10 markah)

(c) Hidrolisis lengkap suatu heksapeptida memberi 2 Gly, Leu, Phe, Pro dan Tyr. Tindak balas peptida tersebut dengan fenilisotiosianat memberi feniltiohidantoin bagi Pro. Hidrolisis separa peptida tersebut memberi serpihan berikut: Phe-Gly-Tyr, Gly-Phe-Gly, Pro-Leu-Gly, Leu-Gly-Phe. Apakah struktur peptida tersebut?

(6 markah)

...17/-

7. (a) Tunjukkan bagaimana anda mensintesis sisteina daripada:



sisteina

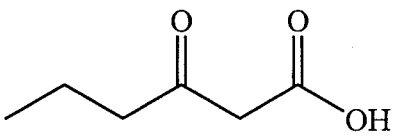
(i) Pengaminan reduktif.

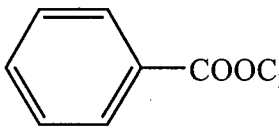
(ii) Sintesis Strecker.

(10 markah)

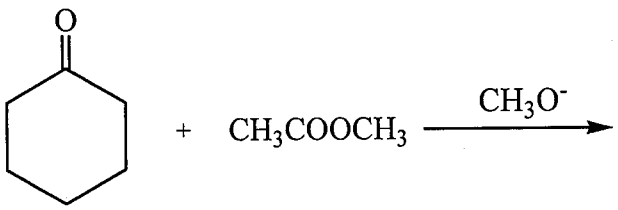
(b) Ramalkan hasil organik utama untuk tindak balas berikut:

(i) $CH_2(CO_2CH_3)_2$ → (1. $NaOCH_3$; 2. $BrCH_2CH_2CH_2CH_2Br$; 3. $NaOCH_3$; 4. H_3O^+, pemanasan)

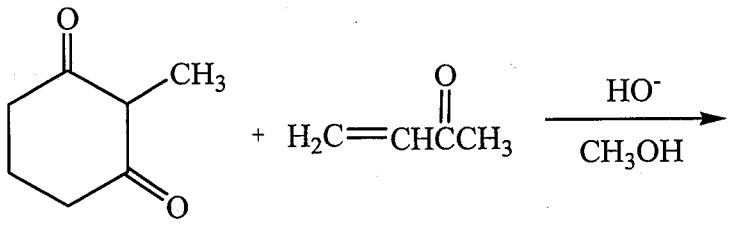
(ii)  → (pemanasan)

(iii)  $+ CH_3COOC_2H_5$ → ($C_2H_5O^-$)

(iv)



(v)



(10 markah)